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(54) Title: **PROCESS FOR POLYMERIZING CATIONICALLY POLYMERIZABLE MONOMERS**

(57) Abstract: The invention relates to a new catalyst system that improves the heat transfer capability of a isobutylene reactor slurry process system in the production of isoolefin homopolymers in continuous slurry polymerization processes. The process is carried out in an anhydrous polymerization system containing a mixture of the monomers in a polar diluent along with a Lewis acid and a C₅ or greater initiator having a tertiary halide.

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**TITLE: PROCESS FOR POLYMERIZING CATIONICALLY
POLYMERIZABLE MONOMERS**

FIELD OF INVENTION

5 The present invention relates to an improved method for production of homopolymers of isobutylene useful in rubber compounds, and more particularly to a method of producing homopolymers of isobutylene at a relatively high slurry concentration within a continuous slurry reactor.

10 **BACKGROUND**

 Homopolymers of isobutylene are well known and their synthesis and properties are described by *Kresge and Wang* in 8 KIRK-OTHMER ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY 934-955 (4th ed. 1993). Isobutylene was initially oligomerized in the 1870s, but it was not until the 1930s that a method of
15 polymerization was developed which produced high molecular weight polyisobutylene (Plesch, P.H., CATIONIC POLYMERIZATION AND RELATED COMPLEXES (Academic: New York, NY, 1953)). These polymers exhibit rubber-like properties by virtue of their high molecular weight; however, they lack suitable functionality for vulcanization. These polymers are commercially
20 available today under the trade names of VISTANEX™ and OPPANOL™. Their chief applications include adhesives, caulks, sealants and chewing gum. Lewis Acids such as the aluminum alkyls and aluminum chloride together with initiators such as water and anhydrous HCl are used extensively in both laboratory experiments and commercial scale production. For economic reasons, it's
25 preferred to produce these polymers at the highest slurry concentration, conversion and production rate sustainable.

 The polymers are made by a cationic slurry polymerization process at approximately -95°C using a catalyst comprising a Lewis Acid and an initiator.
30 Initiators such as water and anhydrous HCl are used extensively. Related patents are EP 0 279 456; WO 00/40624; U.S. 4,385,560, 5,169,914, and 5,506,316, herein incorporated by reference.

The commercial reactors used to make these rubbers are well mixed vessels of greater than 10 to 30 liters in volume with a high circulation rate provided by a pump impeller. The polymerization and the pump both generate heat and, in order to keep the slurry cold, the reactor contains a heat exchanger. One embodiment of such a continuous flow stirred tank reactor ("CFSTR") is found in U.S. Patent No. 5,417,930, incorporated by reference, hereinafter referred to in general as a "reactor" or "isobutylene-type reactor". In these reactors, slurry (reacted monomers) is circulated through tubes of a heat exchanger by a pump, while boiling ethylene on the shell side provides cooling, the slurry temperature being determined by the boiling ethylene temperature, the required heat flux and the overall resistance to heat transfer. On the slurry side, the heat exchanger surfaces progressively foul, often referred to as film fouling, which causes the slurry temperature to rise. This often limits the practical slurry concentration that can be used in most reactors from 18 to 24 wt% relative to the total weight of the slurry, diluent, and unreacted monomers.

As the slurry temperature increases, there is evidence that the slurry viscosity rises, causing a measurable reduction in the heat transfer coefficient and a further increase in slurry temperature. The increase in temperature will cause a further increase in viscosity and the progression continues until the slurry becomes unstable and starts to agglomerate which can lead to reactor plugging. Consequently, reactors experiencing rapid warm up, often referred to as run away, are taken out of service quickly to avoid fouling and plugging, and subsequent plant upsets.

Reactor "warm-up" then refers to the gradual rise in the temperature of the reactor as a polymerization run progresses. At a constant polymerization rate, the warm-up is the result of a progressive loss of heat removal capability in the reactor. The heat removed from the reactor can be represented mathematically by the following equation (1):

$$Q = (U) (A) (T_{\text{slurry}} - T_{\text{ethylene}}) \quad (1)$$

where "Q" is the heat removed, "A" is the surface area of the reactor, "U" is the overall heat transfer coefficient, which is a composite of several heat transfer coefficients for the slurry itself, the walls of the reactor, the film formed on the reactor wall, and the boiling ethylene used to draw heat from the exothermic polymerization reaction. The "T" values are the temperatures of the slurry and ethylene, respectively.

In the polymerization process, the temperature difference driving force for heat transfer must increase if (a) the overall heat transfer coefficient U decreases, and/or (b) the heat transfer area is lost during a reactor run, such as by plugged tubes. Both can occur as a result of film formation and mass fouling of the reactor. Also, U will decrease if the reactor circulation rate drops or the slurry viscosity increases. Although not wishing to be bound by the following mathematical relationship, the slurry side heat transfer coefficient can be related to the viscosity of the slurry by the Sieder-Tate equation for turbulent fluid flow as shown below in equation (2):

$$\frac{h_{\text{slurry}} D}{k} = (0.023) \left(\frac{D v \rho}{\mu_b} \right)^{0.8} \left(\frac{\mu_b c_p}{k} \right)^{0.4} \left(\frac{\mu_b}{\mu_w} \right)^{0.167} \quad (2)$$

where h_{slurry} is the slurry side heat transfer coefficient, D is the diameter of the reactor heat transfer tube, k is the thermal conductivity of the reactor polymerizing slurry, v is the average velocity of the slurry inside the tube, ρ is the average density of the slurry, μ_b is the average bulk viscosity of the polymerizing slurry, c_p is the specific heat of the polymerizing slurry, and μ_w is the average wall viscosity of the polymerizing slurry. Therefore, h_{slurry} is proportional to $(1/\mu_b)^{0.4}$ in equation (2).

Operating problems associated with using these reactors vary depending upon the specific reaction taking place and the specific location within the reactor. One problem with these reactors is the presence of non-homogenous zones beneath (or above) the pump impeller where feed is introduced. The monomer-rich zone adjacent the pump can be particularly troublesome because feed may be introduced with as high as 40% monomer concentration, whereas the steady-state monomer level in the reactor is much lower, typically from 0.1% to 10%. The inventors have found that, surprisingly, if an initiator such as a C₅ or greater tertiary halo-alkyl is added to the system, the reactor heat transfer efficiency improves, consistent with a reduction in viscosity of the slurry. This is unexpected.

Certain tertiary alkyl halide initiators such as tert-butylchloride (a C₄ tertiary halide) have been shown by *Kennedy et al.* in U.S. Patent No. 3,560,458 to improve isobutylene/isoprene polymerization in small scale, batch experiments when compared to HCl. Yet, there is little to no improvement when comparing tert-butylchloride and TMPCl in small scale batch experiments. Further, the lack of steady state conditions in the small batch process means that heat transfer and viscosity changes would not be apparent when going to a continuous, slurry process, nor would the associated problem of reactor fouling. Thus, it would be unexpected that the use of an initiator would improve the production of polyisobutylene on a plant scale.

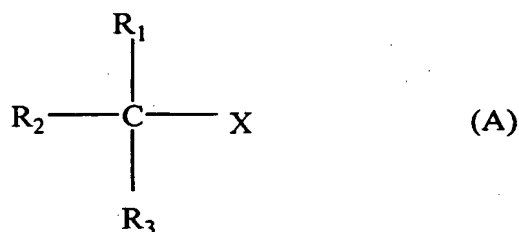
The inventors have unexpectedly found that certain alkyl halide compounds greater than C₄ significantly reduces reactor fouling associated with using HCl as an initiator for polyisobutylene polymerization in continuous slurry reactors. The present invention enables a higher slurry concentration and/or longer run lengths than would otherwise be practical in most commercial reactors.

SUMMARY OF THE INVENTION

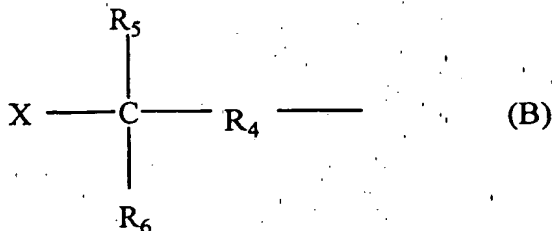
Thus, an object of the present invention is to provide a method of improving heat transfer within a polyisobutylene reactor by employing an improved catalyst system for the polymerization of isoolefins.

The improved catalyst system comprises a Lewis Acid and an initiator that improves heat transfer from the polymerizing slurry to the heat exchanging system built into the reactor by lowering the heat transfer coefficient of the slurry. This will ultimately lower the fouling rate, and allow higher concentrations of monomer to be injected into the reactor and higher slurry concentrations to be maintained, and/or allow the reactor to run for a longer period of time before washing, thus improving the commercial value of the product and process.

An embodiment of the present invention is a method of improving the heat transfer capability within a continuous slurry polymerization reactor in preparing polymers of isoolefin monomers, the reacted monomers forming a slurry within the reactor. The method comprises reacting in a polar diluent the isoolefin, a Lewis acid, and an initiator, wherein the initiator has the formula:



wherein X is a halogen; R_1 is selected from the group consisting of C_1 to C_8 alkyl, and C_2 to C_8 alkenyl; R_3 is selected from the group consisting of C_1 to C_8 alkyl, C_2 to C_8 alkenyl and phenylalkyl; and R_2 is selected from the group consisting of C_4 to C_{200} alkyl, C_2 to C_8 alkenyl, phenyl phenylalkyl, alkylphenyl, C_3 to C_{10} cycloalkyl, and



wherein X is a halogen; R₅ is selected from the group consisting of C₁ to C₈ alkyl, and C₂ to C₈ alkenyl; R₆ is selected from the group consisting of C₁ to C₈ alkyl, C₂ to C₈ alkenyl and phenylalkyl; and R₄ is selected from the group consisting of phenylene, biphenyl, α,ω-diphenylalkane and --(CH₂)_n--, wherein n is an integer from 1 to 10; and wherein R₁, R₂, and R₃ can also form adamantyl or bornyl ring systems, the X group being in a tertiary carbon position. Further, the slurry within the reactor is in a concentration of 50 wt% or less in one embodiment.

DETAILED DESCRIPTION

The invention concerns a catalyst system and process for production of isoolefin homopolymers. An improved catalyst system and process has been discovered which affords many unexpected advantages for commercial slurry polymerization processes. The discussion and examples below are focused on embodiments of the broad invention. To the extent that the description is specific, this is done solely for the purpose of illustrating exemplifying embodiments and should not be taken as restricting the invention to these embodiments.

The polymerization system of the invention contains monomers, a Lewis acid catalyst, an initiator, and a polar diluent. The polymerization reactor is maintained substantially free of impurities, which can complex with the catalyst, the initiator, or the monomers, and the polymerization reaction is conducted under conditions to limit or avoid chain transfer and termination of the growing polymer chains. Anhydrous conditions are highly preferred and reactive impurities, such as components containing active hydrogen atoms (water, alcohol and the like)

must be removed from both the monomer and diluents by techniques well-known in the art.

Definition of Terms

5 As used herein, the term "catalyst system" refers to and includes any Lewis Acid or other metal complex used to catalyze the polymerization of the olefinic monomers of the invention, as well as the initiator described below, and other minor catalyst components.

10 As used herein, the "polymerization system" is the catalyst system and the monomers and reacted monomers within the isobutylene-type reactor.

As used herein, the term "slurry" refers to reacted monomers that have polymerized to a stage that they have precipitated from the diluent. The slurry
15 "concentration" is the weight percent of these reacted monomers--the weight percent of the reacted monomers by total weight of the slurry, diluent, unreacted monomers, and catalyst system.

As used herein, the new numbering scheme for the Periodic Table Groups
20 are used as in HAWLEY'S CONDENSED CHEMICAL DICTIONARY 852 (13th ed. 1997).

Monomers

Polyisooolefin rubber is produced by the polymerization reaction between
25 isooolefin monomers. The olefin polymerization feeds employed in connection with the catalyst and initiator system (described in more detail below) are those olefinic compounds, the polymerization of which are known to be cationically initiated, and are free of aromatic monomers such as para-alkylstyrene monomers. Preferably, the olefin polymerization feeds employed in the present invention are
30 those olefinic compounds conventionally used in the preparation of isobutylene-type rubber polymers. The homopolymers are prepared by reacting monomers of a C₄ to C₆ isooolefin monomer component such as isobutene.

In one embodiment, the isoolefin is a C₄ to C₆ compound such as isobutylene, isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, and 4-methyl-1-pentene. Desirably, the isoolefin is isobutylene.

Lewis Acid

An isomonoolefin, in particular isobutylene, can be homopolymerized under cationic conditions. The polymerization is carried out by means of a Lewis Acid catalyst. Embodiments of the invention include Lewis Acid catalysts (including Friedel-Crafts catalysts) which show good polymerization activity. Desirable catalysts are Lewis Acids based on metals from Group 4, 13 and 15 of the Periodic Table of the Elements, including boron, aluminum, gallium, indium, titanium, zirconium, tin, vanadium, arsenic, antimony, and bismuth. In one embodiment, the metals are aluminum, boron and titanium, with aluminum being desirable. In the practice of the method of this invention, weaker acids are preferred as they lead to less alkylation and branching and higher monomer conversion rates.

The Group 13 Lewis Acids have the general formula R_nMX_{3-n}, wherein "M" is a Group 13 metal, R is a monovalent hydrocarbon radical selected from the group consisting of C₁ to C₁₂ alkyl, aryl, arylalkyl, alkylaryl and cycloalkyl radicals; and *n* is an integer from 0 to 3; X is a halogen independently selected from the group consisting of fluorine, chlorine, bromine, and iodine, preferably chlorine. The term "arylalkyl" refers to a radical containing both aliphatic and aromatic structures, the radical being at an alkyl position. The term "alkylaryl" refers to a radical containing both aliphatic and aromatic structures, the radical being at an aryl position. Nonlimiting examples of these Lewis acids include aluminum chloride, aluminum bromide, boron trifluoride, boron trichloride, ethyl aluminum dichloride (EtAlCl₂ or EADC), diethyl aluminum chloride (Et₂AlCl or DEAC), ethyl aluminum sesquichloride (Et_{1.5}AlCl_{1.5} or EASC), trimethyl aluminum, and triethyl aluminum.

The Group 4 Lewis Acids have the general formula MX_4 , wherein M is a Group 4 metal and X is a ligand, preferably a halogen. Nonlimiting examples include titanium tetrachloride, zirconium tetrachloride, or tin tetrachloride.

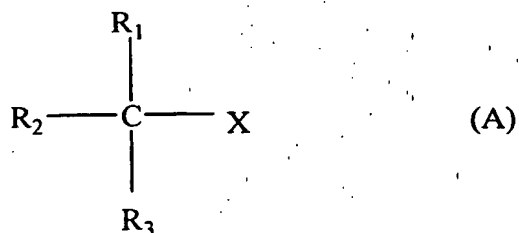
5 The Group 15 Lewis Acids have the general formula MX_y , wherein M is a Group 15 metal, X is a ligand, preferably a halogen, and y is an integer from 3 to 5. Nonlimiting examples include vanadium tetrachloride and antimony pentafluoride.

10 Particularly preferred Lewis acids may be any of those useful in cationic polymerization of isobutylene polymers including: $AlCl_3$, EADC, EASC, DEAC, BF_3 , $TiCl_4$, etc. with EASC and EADC being especially preferred.

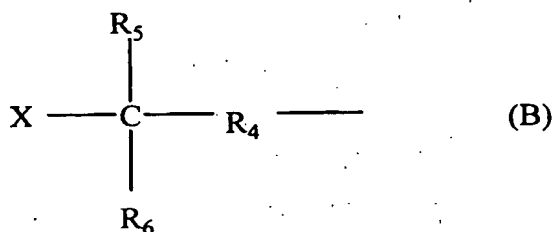
15 Catalyst efficiency (based on Lewis Acid) in the reactor is maintained between 10000 lb. of polymer/lb. of catalyst and 300 lb. of polymer/lb. of catalyst and desirably in the range of 5000 lb. of polymer/lb. of catalyst to 1000 lb. of polymer/lb. of catalyst by controlling the molar ratio of Lewis Acid to initiator.

Initiator

20 According to a desirable embodiment of the invention, the Lewis Acid catalyst is used in combination with an initiator. The initiators are those which are capable of being precomplexed in a suitable diluent with the chosen Lewis Acid to yield a mixture suitable for propagating a polymer chain. These initiators yield a fast, simple initiation of polymerization in the reactor as opposed to the slow
25 stepwise initiations involving several polar complexes in equilibrium characteristic of the catalyst systems such as water or HCl initiators conventionally used in commercial cationic slurry polymerization of isobutylene. The initiator is a tertiary halide greater than C_4 , wherein the initiator has the formula (A):

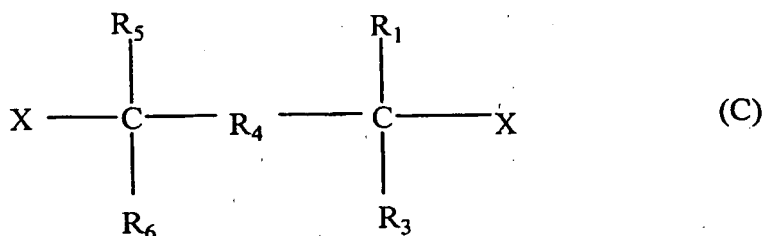


wherein X is a halogen; R_1 is selected from the group consisting of C_1 to C_8 alkyl, and C_2 to C_8 alkenyl; R_3 is selected from the group consisting of C_1 to C_8 alkyl, C_2 to C_8 alkenyl and phenylalkyl; and R_2 is selected from the group consisting of C_4 to C_{200} alkyl, C_2 to C_8 alkenyl, phenyl, phenylalkyl, alkylphenyl, C_3 to C_{10} cycloalkyl, and



wherein X is a halogen; R_5 is selected from the group consisting of C_1 to C_8 alkyl, and C_2 to C_8 alkenyl; R_6 is selected from the group consisting of C_1 to C_8 alkyl, C_2 to C_8 alkenyl and phenylalkyl; and R_4 is selected from the group consisting of phenylene, biphenyl, α,ω -diphenylalkane and $-(CH_2)_n-$, wherein n is an integer from 1 to 10; and wherein R_1 , R_2 , and R_3 can also form adamantyl or bornyl ring systems, the X group being in a tertiary carbon position.

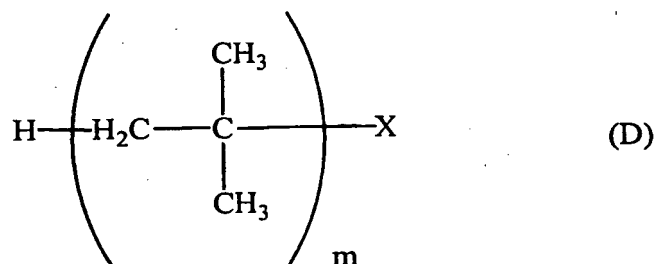
Substitution of the above structural formula radical (B) for R_2 in formula (A) results in the following formula (C):



wherein X, R₁, R₃, R₄, R₅ and R₆ are as defined above. The compounds represented by structural formula (C) contain two dissociable halides and may be considered as merely multiples of those compounds represented by structural formula (A).

Multifunctional initiators are employed where the production of branched polymers is desired, while mono- and di-functional initiators are preferred for the production of substantially linear polymers.

In one desirable embodiment of structure (A), the initiator is an oligomer of isobutylene as in structure (D):



wherein X is a halogen, and the value of m is from 1 to 60, and mixtures thereof. In another embodiment, m is from 2 to 40. This structure is also described as a tertiary alkyl chloride-terminated polyisobutylene having a Mn up to 2500 in one embodiment, and up to 1200 in another embodiment.

Non-limiting examples of suitable initiators are cumyl esters of hydrocarbon acids, and alkyl cumyl ethers. Representative initiators, for example, comprise compounds such as 2-acetyl-2-phenylpropane, i.e., cumyl acetate; 2-methoxy-2-phenyl propane, i.e., cumylmethyl-ether; 1,4-di(2-methoxy-2-

propyl)benzene, i.e., di(cumylmethyl ether); the cumyl halides, particularly the chlorides, i.e., 2-chloro-2-phenylpropane, i.e., cumyl chloride (1-chloro-1-methylethyl)benzene; 1,4-di(2-chloro-2-propyl)benzene, i.e., di(cumylchloride); 1,3,5-tri(2-chloro-2-propyl)benzene, i.e., tri(cumylchloride); the aliphatic halides, particularly the chlorides, i.e., 2-chloro-2,4,4-trimethylpentane (TMPCl), 2-bromo-2,4,4-trimethylpentane (TMPBr), 2,6-dichloro-2,4,4,6-tetramethylheptane; cumyl and aliphatic hydroxyls such as 1,4-di((2-hydroxyl-2-propyl)-benzene), 2,6-dihydroxyl-2,4,4,6-tetramethyl-heptane, 1-chloroadamantane and 1-chlorobornane, 5-tert-isobutylene-1,3-di(1-chloro-1-methyl ethyl) benzene and similar compounds. Other suitable initiators may be found in U.S. Patent No. 4,946,899, herein incorporated by reference for purposes of U.S. patent practice. These initiators are generally C₅ or greater tertiary or allylic alkyl or benzylic halides and may include polyfunctional initiators. Desirable examples of these initiators include: TMPCl, TMPBr, 2,6-dichloro-2,4,4,6-tetramethylheptane, cumyl chloride as well as 'di-' and 'tri-' cumyl chloride or bromide. In another embodiment, the initiator is a tertiary alkyl chloride-terminated polyisobutylene with a Mn (number average molecular weight) up to 2500.

In one embodiment, the TMPCl is made by dissolving isobutylene dimer in methylchloride and then adding anhydrous HCl to form the alkyl chloride. Excess HCl is then purged by nitrogen and the resulting solution of TMPCl in methylchloride is used as the initiator stream in a continuous plant to make isobutylene polymers. In one embodiment of the commercial-type process, the TMPCl stream is mixed with a cold methylchloride (chloromethane) stream and an aluminum alkyl stream to form the catalyst system. This stream is then injected into the continuous flow stirred tank reactor ("CFSTR") used to produce isobutylene polymers under much more controllable and economic conditions than has previously been possible. In another embodiment, isobutylene dimers are reacted with HCl inline and then fed directly into the reactor.

Polymerisation Reaction Conditions

The selected diluent or diluent mixture should provide a diluent medium having some degree of polarity in order for the polymerization to proceed at a reasonable rate. To fulfil this requirement, a mixture of nonpolar and polar diluents can be used. In the alternative, a mixture of, or a single polar diluent, is more desirable. Suitable nonpolar diluent components includes hydrocarbons and preferably aromatic or cyclic hydrocarbons or mixtures thereof. Such compounds include, for instance, methylcyclohexane, cyclohexane, toluene, carbon disulfide and others. Appropriate polar diluents include halogenated hydrocarbons, normal, branched chain or cyclic hydrocarbons. Specific compounds include the preferred liquid diluents such as ethyl chloride, methylene chloride (dichloromethane, CH_2Cl_2), methylchloride (chloromethane, CH_3Cl), CO_2 , CHCl_3 , CCl_4 , n-isobutylene chloride, chlorobenzene, and other chlorinated hydrocarbons. Methylchloride is desirably used in an embodiment of the invention. To achieve suitable polarity and solubility, it has been found that if the diluent, or diluents, is mixed, the mixture is preferably at least 70 % polar diluent, on a volume basis.

As is normally the case, product molecular weights are determined by reaction time, temperature, concentration, the nature of the reactants, and similar factors. Consequently, different reaction conditions will produce products of different molecular weights. Synthesis of the desired reaction product will be achieved, therefore, through monitoring the course of the reaction by the examination of samples taken periodically during the reaction, a technique widely employed in the art and shown in the examples or by sampling the effluent of a continuous reactor.

The reactors that may be utilized in the practice of the present invention include any conventional reactors and equivalents thereof capable of performing a continuous slurry process, such as disclosed in U.S. 5,417,930, herein incorporated by reference. The reactor pump impeller can be of the up-pumping variety or the down-pumping variety. The reactor will contain sufficient amounts of the catalyst system of the present invention effective to catalyze the

polymerization of the monomer containing feed-stream such that a sufficient amount of polymer having desired characteristics is produced. The feed-stream in one embodiment contains a total monomer concentration greater than 30 wt% (based on the total weight of the monomers, diluent, and catalyst system), greater than 35 wt% in another embodiment. In yet another embodiment, the feed-stream will contain from 35 wt% to 50 wt% monomer concentration based on the total weight of monomer, diluent, and catalyst system.

The feed-stream is substantially free from silica cation producing species. By substantially free of silica cation producing species, it is meant that there is no more than 0.0005 wt% based on the total weight of the monomers of these silica species in the feed stream. Typical examples of silica cation producing species are halo-alkyl silica compounds having the formula $R_1R_2R_3SiX$ or $R_1R_2SiX_2$, etc., wherein "R" is an alkyl and "X" is a halogen. Finally, the feed stream should be free of aromatic-containing monomers such as para-alkylstyrene.

The reaction conditions will be such that desirable temperature, pressure and residence time are effective to maintain the reaction medium in the liquid state and to produce the desired polymers having the desired characteristics. The monomer feed-stream is typically substantially free of any impurity which is adversely reactive with the catalyst under the polymerization conditions. For example, the monomer feed preferably should be substantially free of bases (such as caustic), sulfur-containing compounds (such as H_2S , COS , and organo-mercaptans, e.g., methyl mercaptan, ethyl mercaptan), N-containing compounds, oxygen containing bases such as alcohols and the like.

The polymerization reaction temperature is conveniently selected based on the target polymer molecular weight and the monomer to be polymerized as well as standard process variable and economic considerations, e.g., rate, temperature control, etc. The temperature for the polymerization is between $-10^{\circ}C$ and the freezing point of the polymerization system in one embodiment, and from $-25^{\circ}C$ to $-120^{\circ}C$ in another embodiment. In yet another embodiment, the polymerization

temperature is from -40°C to -100°C , and from -70°C to -100°C in yet another embodiment. In yet another desirable embodiment, the temperature range is from -80°C to -100°C . The temperature is chosen such that the desired polymer molecular weight is achieved. The reaction pressure will be from 200 kPa to 1600 kPa in one embodiment, from 300 kPa to 1200 kPa in another embodiment, and from 400 kPa to 1000 kPa in yet another embodiment.

The catalyst (Lewis Acid) to monomer ratio utilized will be those conventional in this art for carbocationic polymerization processes. In one embodiment of the invention, the catalyst to monomer mole ratios will be from 0.10 to 20, and in the range of 0.5 to 10 in another embodiment. In another desirable embodiment, the ratio of Lewis Acid to initiator is from 0.1 to 10 in one embodiment, from 0.75 to 5 in another embodiment, and from 1.1 to 2.0 in yet another embodiment. The polymer to initiator ratio can be from 1 to 10 in one embodiment, and from 1.5 to 2 in another embodiment. The catalyst efficiency, or the kg polymer/kg Lewis Acid, is from 1000 to 15,000 in one embodiment, and from 2000 to 6000 in another embodiment. The overall concentration of the initiator is from 50 to 300 ppm within the reactor in one embodiment, and from 100 to 250 ppm in another embodiment. The concentration of the initiator in the catalyst feed stream is from 500 to 3000 ppm in one embodiment, and from 1000 to 2500 in another embodiment. Another way to describe the amount of initiator in the reactor is by its amount relative to the polymer. In one embodiment, there is from 0.25 to 5.0 moles polymer/mole initiator, and from 0.5 to 3.0 mole polymer/mole initiator in another embodiment.

The reacted monomers within the reactor form a slurry. The term "slurry" refers to reacted monomers that have polymerized to a stage that they have precipitated from the diluent. The slurry "concentration" is the weight percent of these reacted monomers--the weight percent of the reacted monomers by total weight of the slurry, diluent, unreacted monomers, and catalyst system. In one embodiment, the concentration of the slurry is equal to or greater than 10 wt%. In another embodiment, the slurry is present in the reactor in a concentration equal

to or greater than 18 wt%. In yet another embodiment, the slurry concentration in the reactor is less than or equal to 50 wt%. In yet another embodiment, the slurry is present in the reactor from 18 to 50 wt%. And in yet another embodiment, the slurry concentration is present in the reactor from 30 to 40 wt%.

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The slurry is characterized by having a heat transfer coefficient (h_{slurry}) as defined above in equation (2). In one embodiment of the invention, the heat transfer coefficient of the slurry is from 200 to 500 Btu/hr-ft²·°F. In another embodiment of the invention, the heat transfer coefficient of the slurry is from 300 to 450 Btu/hr-ft²·°F.

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The order of contacting the monomer feed-stream, catalyst, initiator, and diluent is not critical to this invention. In one embodiment, the initiator and Lewis Acid are pre-complexed by mixing together in cold methylchloride or other suitable cold polar diluent, immediately before injection into the continuous reactor through a catalyst nozzle in the standard way. Other methods may also be employed that will inject the initiator into the reactor. Desirably, the monomer is not contacted with the Lewis Acid and initiator before entering the reactor.

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In an embodiment of the invention, the initiator and Lewis Acid are allowed to pre-complex by mixing together in cold methylchloride at temperatures between -50°C and -98°C with a contact time between 0.5 seconds and several hours, and between 1 second and 5 minutes before injection into the reactor in another embodiment. In yet another embodiment, Lewis Acid and the initiator are added to the reactor separately.

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In one embodiment, the polymerization of isobutylene to form polyisobutylene comprises several steps. First, a reactor having a pump impeller capable of up-pumping or down-pumping is provided. The pump impeller is typically driven by an electric motor with a measurable amperage. The reactor typically is equipped with parallel vertical reaction tubes within a jacket containing liquid ethylene. The total internal volume, including the tubes, is

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greater than 30 to 50 liters in one embodiment, and from 6400 liters to 7600 in yet another embodiment, thus capable of large scale volume polymerization reactions. The reactor typically uses liquid ethylene to draw the heat of the polymerization reaction away from the forming slurry. The pump impeller keeps a constant flow of slurry, diluent, catalyst system and unreacted monomers through the reaction tubes. A feed-stream of the isobutylene in a polar diluent is charged into the reactor, the feed-stream containing less than 0.0005 wt% of cation producing silica compounds, and typically free of aromatic monomers. The catalyst system is then charged into the feed-stream, the catalyst system having a Lewis acid and an initiator present in a molar ratio of from 0.50 to 10.0. Within the reactor, the feed-stream of monomers and catalyst system are allowed to contact one another, the reaction thus forming a slurry of polyisobutylene, wherein the slurry has a concentration of from 25 wt% to 50 wt%. Finally, the thus formed polyisobutylene is allowed to exit the reactor through an outlet or outflow line while simultaneously allowing the feed-stream charging to continue, thus constituting the continuous slurry polymerization. Advantageously, the present invention improves this process in a number of ways, ultimately reducing the amount of clogging that occurs in the exit port which is measured by pressure inconsistencies or "jumps".

The overall residence time in the reactor can vary, depending upon, e.g., catalyst activity and concentration, monomer concentration, feed injection rate, production rate, reaction temperature, and desired molecular weight, and generally will be between about one minute and five hours, and preferably between about 10 and 60 minutes. The principle variable controlling residence time is the monomer feed injection rate. The resultant polymer from one embodiment of the invention is a polyisobutylene polymer that has a molecular weight distribution of from about 2 to 5, and an unsaturation of from 0.5 to 2.5 mole per 100 mole of monomer.

In a desirable embodiment of the present invention, a homopolymer of isobutylene is produced. Polyisobutylenes are sold commercially under the name

VISTANEX™ by ExxonMobil Chemical Company (Houston, TX). The commercial polyisobutylene polymers range from low molecular weight semiliquids (Mv of 50,000 to 90,000) to high molecular weight elastomers (Mv > 500,000).

5

The new catalyst system and process affords many unexpected advantages for commercial slurry polymerization of isoolefins. The improvements obtained with this new initiator are demonstrated in commercial plant scale tests. The following examples reflect embodiments of the invention and are by no means intended to be limiting of the scope of the invention.

10

Examples

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Table 1 includes two example runs of polyisobutylene production in plant scale reactions. In these runs, the Lewis Acid is EADC the initiator is HCl that are blended at a molar ratio of 4.0. Butene is added to the reaction to reduce polymerization around the area where monomer feed is introduced into the reactor. Dimers are used for control of the molecular weight by chain transfer.

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The use of an initiator as described above, such as for example TMPCl would reduce the need for butene and lower the reaction warm-up rate. The use of TMPCl will increase the heat transfer of the slurry and will allow the slurry concentration to be run up to 25%, thus increasing production by greater than 5%. Also, mass fouling around the pump in the feed inlet zone will be reduced, thus allowing the reactors to be run at higher rates or for longer periods of time, thus increasing production additionally by 1 to 2%. Also, fouling on the heat transfer surfaces in the reactor will be reduced, which will reduce overflow kickings.

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The Lewis acid efficiency (kg polymer/kg Lewis acid) is expected to be between about 1000 and 15,000, and the moles of polymer produced per mole of initiator will be from 1.5 to 2 in one embodiment, while the ratio of EADC to TMPCl will be from 1.1 to 2 in one embodiment.

Discussion

5 The present invention has several advantages. Because of the rapid reactor mass fouling rate that typically occurs, reactors had to be operated at very low slurry concentrations and heat loads to achieve the run lengths required to allow washing and turnaround to be accomplished in the time available before the fouled reactor had to be put back into production to replace another fouled reactor. The present invention, as shown in the examples, will allow the isobutylene reactors to
10 be run at higher slurry concentrations and/or run at a lower concentration for a longer period of time before fouling. In one embodiment of the invention, the run length is increased from 30 % to 200 % relative to the run length when HCl or C₄ or smaller initiators are used in the catalyst system.

15 Embodiments of the invention improve the heat transfer within the reactor. The improved heat transfer can allow either higher slurry concentrations, or longer run length. The heat transfer coefficient is thus higher due to the lower viscosity of the slurry as would be predicted using the Sieder-Tate equation for turbulent flow. Further, there is a lower overflow line plugging rate with embodiments of
20 the present invention and steadier reactor operation due to the lower pump power consumption. Also, since heat transfer is improved, longer run lengths at relatively low slurry concentrations (below 25 wt%) are possible since it is known that the reactor will stay cold (liquid ethylene temperatures) for longer when the heat transfer coefficient of the slurry is low. The cooler temperatures lower the
25 fouling rate of the heat transfer surfaces, thus allowing the reactor to stay on line without stoppage for cleaning for a longer period of time that was previously possible.

30 All priority documents are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted. Further, all documents cited herein, including testing procedures, are herein fully incorporated by reference for all jurisdictions in which such incorporation is permitted.

Table 1. Plant scale reaction conditions for polyisobutylene production

Parameter	Stick Temp (°C)	Shoot Temp (°C)	Rxn Warm-up Rate (°C/hr)	Rxn Feed Rate (kg/hr)	iC4= Conversion (%)	Cat Efficiency (kg/kg) ¹	EADC/HCl Molar Ratio (mol/mol)	Dimer to iC4= Ratio (lb/100lb) ²	iC4= Conc. in FB ³ (wt%)	Total Butene Conc. in FB (wtppm) ⁴
Run 1	-96.6	-92.6	0.046	8391	99.1	3122	4.0	0.47	22.0	597
Run 2	-97.0	-93.5	0.061	8391	99.3	4036	4.0	0.46	22.0	602

Note: 1. kg EADC/kg polymer

2. The dimer is added to increase chain transfer and control molecular weight.

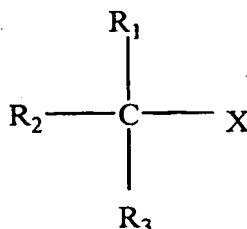
3. FB is feed blend.

4. The butenes are added to reduce polymerization around the feed slot (wtppm is weight ppm).

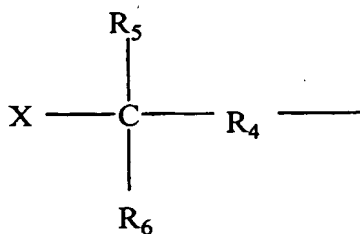
CLAIMS

We claim:

1. A polymerization method for use in a continuous slurry polymerization reactor in preparing a homopolymer of an isoolefin, the reacted monomers forming the slurry within the reactor, a Lewis acid, and an initiator, wherein the initiator has the formula:



wherein X is a halogen; R₁ is selected from the group consisting of C₁ to C₈ alkyl, and C₂ to C₈ alkenyl; R₃ is selected from the group consisting of, C₁ to C₈ alkyl, C₂ to C₈ alkenyl and phenylalkyl; and R₂ is selected from the group consisting of C₄ to C₂₀₀ alkyl, C₂ to C₈ alkenyl, phenyl, phenylalkyl, alkylphenyl, C₃ to C₁₀ cycloalkyl, and



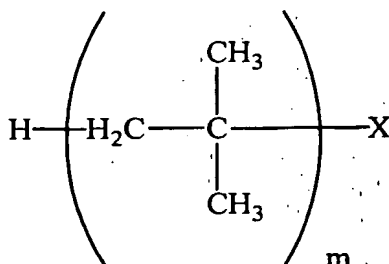
wherein X is a halogen; R₅ is selected from the group consisting of, C₁ to C₈ alkyl, and C₂ to C₈ alkenyl; R₆ is selected from the group consisting of, C₁ to C₈ alkyl, C₂ to C₈ alkenyl and phenylalkyl; and R₄ is selected from the group consisting of phenylene, biphenyl, α,ω-diphenylalkane and --(CH₂)_n--, wherein n is an integer from 1 to 10; and wherein R₁, R₂, and R₃ can also form adamantyl or bornyl ring systems, the X group being in a tertiary carbon position.

2. The method of Claim 1, wherein the Lewis acid is a metal halide based on a metal selected from the group consisting of tin, titanium, aluminum, boron, and a mixture thereof.
- 5 3. The method of Claim 2, wherein the metal halide is selected from the group consisting of aryl aluminum halides, alkyl-substituted aryl aluminum halides, alkyl aluminum halides and a mixture thereof.
- 10 4. The method of Claim 2, wherein the metal halide is selected from the group consisting of dialkyl aluminum halide, monoalkyl aluminum dihalide, aluminum tri-halide, ethylaluminum sesquichloride, and a mixture thereof.
- 15 5. The method of Claim 2, wherein the metal halide is selected from the group consisting of AlCl_3 , EtAlCl_2 , $\text{Et}_{1.5}\text{AlCl}_{1.5}$, Et_2AlCl , and mixtures thereof.
- 20 6. The method of Claim 1, wherein the reaction is performed at a temperature in the range of from -30°C to the freezing point of the diluent.
7. The method of Claim 1, wherein the reaction is performed at a temperature in the range of from -70°C to -100°C .
- 25 8. The method of Claim 1, wherein the initiator is selected from the group consisting of:
2-chloro-2-phenylpropane;
1,4-di(2-chloro-2-propyl)benzene;
1,3,5-tri(2-chloro-2-propyl)benzene;
3-tert-isobutylene-1,5-di(2-chloro-2-propyl)benzene;
30 2-chloro-2,4,4-trimethylpentane;
2-bromo-2,4,4-trimethylpentane;
1-chloroadamantane;

1-chlorobornane;
cumyl chloride;
2,6-dichloro-2,4,4,6-tetramethylheptane and mixtures thereof.

- 5 9. The method of Claim 1, wherein the ratio of the Lewis acid to the initiator
 on a molar basis is from 1.1 to 2.
10. The method of Claim 1, wherein the ratio of the Lewis acid to the initiator
 on a molar basis is from 0.75 to 5.0.
- 10 11. The method of Claim 1, wherein the polar diluent is selected from the
 group consisting of CH_3Cl , EtCl_2 , CH_2Cl_2 , CHCl_3 , CO_2 , CCl_4 and mixtures
 thereof.
12. The method of Claim 1, wherein the isoolefin monomer is isobutylene.
- 15 13. The method of Claim 1, wherein the slurry is present in the reactor in a
 range greater than or equal to 18 wt%.
14. The method of Claim 1, wherein the slurry is present in the reactor less
20 than or equal to 50 wt%.
15. The method of Claim 1, wherein the slurry is present in the reactor from
 25 wt% to 50 wt%.
- 25 16. The method of Claim 1, wherein the isoolefin is present in the reactor in a
 range from 30 to 40 wt%.
17. The method of Claim 1, wherein cation producing silica species are
30 substantially absent.

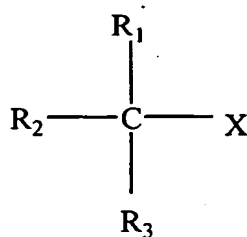
18. The method of Claim 1, wherein the initiator is selected from the group having the formula:



5 wherein X is a halogen and the value of m is from 1 to 60, and mixtures thereof.

19. The method of Claim 20, wherein the initiator has a Mn of up to 2500.

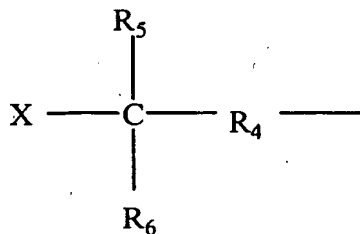
- 10 20. A method of improving the heat transfer capability within a continuous slurry polymerization reactor in preparing a homopolymer of an isoolefin monomer, the reacted monomers forming a slurry within the reactor, the method comprising reacting in a polar diluent the isoolefin monomers, a Lewis acid, and an initiator, wherein the initiator has the formula:



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wherein X is a halogen; R₁ is selected from the group consisting of C₁ to C₈ alkyl, and C₂ to C₈ alkenyl; R₃ is selected from the group consisting of C₁ to C₈ alkyl, C₂ to C₈ alkenyl and phenylalkyl; and R₂ is selected from the group consisting of C₄ to C₂₀₀ alkyl, C₂ to C₈ alkenyl, phenyl, phenylalkyl, alkylphenyl, C₃ to C₁₀ cycloalkyl, and

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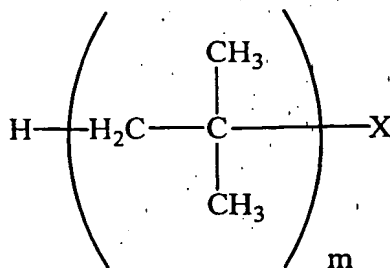


wherein X is a halogen; R₅ is selected from the group consisting of C₁ to C₈ alkyl, and C₂ to C₈ alkenyl; R₆ is selected from the group consisting of C₁ to C₈ alkyl, C₂ to C₈ alkenyl and phenylalkyl; and R₄ is selected from the group consisting of phenylene, biphenyl, α,ω-diphenylalkane and --(CH₂)_n--, wherein n is an integer from 1 to 10; and wherein R₁, R₂, and R₃ can also form adamantyl or bornyl ring systems, the X group being in a tertiary carbon position; and wherein the slurry within the reactor is in a concentration in the range of 50 wt% or less.

21. The method of Claim 20, wherein the heat transfer coefficient of the slurry is from 200 to 500 Btu/hr·ft²·°F.
22. The method of Claim 20, wherein the heat transfer coefficient of the slurry is from 300 to 450 Btu/hr·ft²·°F.
23. The method of Claim 20, wherein the heat transfer coefficient of the slurry is from 375 to 450 Btu/hr·ft²·°F when the slurry concentration is from 25 to 30 wt%.
24. The method of Claim 20, wherein the heat transfer coefficient of the slurry is from 200 to 350 Btu/hr·ft²·°F when the slurry concentration is from 30 to 35 wt%.

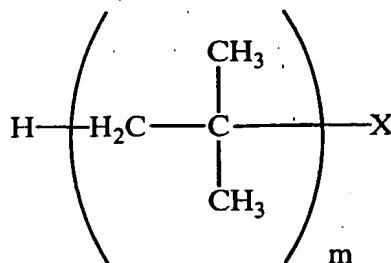
25. The method of Claim 20, wherein the Lewis acid is a metal halide based on a metal selected from the group consisting of tin, titanium, aluminum, boron, and a mixture thereof.
- 5 26. The method of Claim 25, wherein the metal halide is selected from the group consisting of aryl aluminum halides, alkyl-substituted aryl aluminum halides, alkyl aluminum halides and a mixture thereof.
- 10 27. The method of Claim 25, wherein the metal halide is selected from the group consisting of dialkyl aluminum halide, monoalkyl aluminum dihalide, aluminum tri-halide, ethylaluminum sesquichloride, and a mixture thereof.
- 15 28. The method of Claim 25, wherein the metal halide is selected from the group consisting of AlCl_3 , EtAlCl_2 , $\text{Et}_{1.5}\text{AlCl}_{1.5}$, Et_2AlCl , and a mixture thereof.
- 20 29. The method of Claim 20, wherein the reaction is performed at a temperature in the range of from -30°C to the freezing point of the diluent.
30. The method of Claim 20, wherein the initiator is selected from the group consisting of:
2-chloro-2-phenylpropane;
1,4-di(2-chloro-2-propyl)benzene;
25 1,3,5-tri(2-chloro-2-propyl)benzene;
3-tert-isobutylene-1,5-di(2-chloro-2-propyl)benzene;
2-chloro-2,4,4-trimethylpentane;
1-chloroadamantane;
1-chlorobornane;
30 cumyl chloride;
2,6-dichloro-2,4,4,6-tetramethylheptane and mixtures thereof.

31. The method of Claim 20, wherein the ratio of the Lewis acid to the initiator on a molar basis is from 1.1 to 2.
32. The method of Claim 20, wherein the ratio of the Lewis acid to the initiator on a molar basis is from 0.75 to 5.0.
33. The method of Claim 20, wherein the polar diluent is selected from the group consisting of CH_3Cl , EtCl_2 , CH_2Cl_2 , CHCl_3 , CO_2 , CCl_4 and mixtures thereof.
34. The method of Claim 20, wherein the isoolefin monomer is isobutylene.
35. The method of Claim 20, wherein the diluent is CH_3Cl .
36. The method of Claim 20, wherein the reactor run length is increased by from 30 % to 200 % relative to the run length when HCl or a C_4 or smaller initiator is used in the polymerization process.
37. The method of Claim 20, wherein cation producing silica species are substantially absent.
38. The method of Claim 20, wherein the initiator is selected from the group having the formula:



wherein X is a halogen and the value of m is from 1 to 60, and mixtures thereof.

- 5 39. The method of Claim 40, wherein the initiator has a Mn of up to 2500.
40. A method of preparing polyisobutylene, the method comprising reacting in a polar diluent the isoolefin, a Lewis acid, and an initiator, wherein the initiator is selected from the group having the formula:



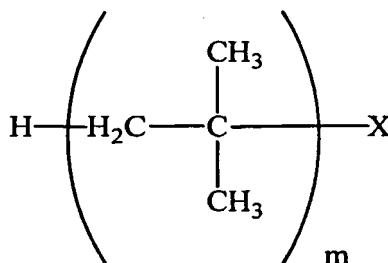
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wherein X is a halogen and the value of m is from 1 to 60, and mixtures thereof, wherein the monomers are reacted in a continuous slurry reactor, the reacted monomers forming a slurry within the reactor.

- 15 41. The method of Claim 40, wherein the slurry is present in the reactor in a range greater than or equal to 18 wt%.
42. The method of Claim 40, wherein the slurry is present in the reactor less than or equal to 50 wt%.

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43. The method of Claim 40, wherein the heat transfer coefficient of the slurry is from 200 to 500 Btu/hr-ft²·°F.
44. The method of Claim 40, wherein the value of m is from 2 to 40.
45. The method of Claim 40, wherein the ratio of the Lewis acid to the initiator on a molar basis is from 1.1 to 2.
46. The method of Claim 40, wherein the ratio of the Lewis acid to the initiator on a molar basis is from 0.75 to 5.0.
47. The method of Claim 40, wherein cation producing silica species are substantially absent.
48. A method of preparing polyisobutylene, the method comprising reacting in a polar diluent isobutylene, a Lewis acid, and an initiator, wherein the initiator is selected from the group having the formula:



- wherein X is a halogen and the value of m is from 1 to 60, and mixtures thereof, wherein isobutylene monomers are reacted in a continuous slurry reactor, the reacted monomers forming a slurry within the reactor.
49. The method of Claim 48, wherein the slurry is present in the reactor in a range greater than or equal to 18 wt%.

50. The method of Claim 48, wherein the slurry is present in the reactor less than or equal to 50 wt%.
51. The method of Claim 48, wherein the heat transfer coefficient of the slurry is from 200 to 500 Btu/hr-ft²-°F.
52. The method of Claim 48, wherein the value of m is from 2 to 40.
53. The method of Claim 48, wherein the polar diluent is selected from the group consisting of CH₃Cl, EtCl₂, CH₂Cl₂, CHCl₃, CO₂, CCl₄ and mixtures thereof.
54. The method of Claim 48, wherein the ratio of the Lewis acid to the initiator on a molar basis, is from 1.1 to 2.
55. The method of Claim 48, wherein the ratio of the Lewis acid to the initiator on a molar basis is from 0.75 to 5.
56. The method of Claim 48, wherein cation producing silica species are substantially absent.
57. A method of preparing polyisobutylene, the method comprising:
- providing a reactor of at least 6400 to 7600 liters in volume and a pump impeller;
- charging a feed-stream of isobutylene in a polar diluent into the reactor, wherein the feed-stream contains less than 0.0005 wt% of cation producing silica compounds; and
- charging a catalyst system into the feed-stream, the catalyst system having a Lewis acid and an initiator present in a molar ratio of from 0.50 to 10.0;

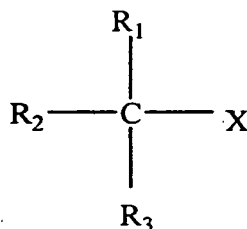
allowing the feed-stream of monomers and catalyst system to contact one another within the reactor, the reaction thus forming a slurry of isobutylene rubber, wherein the slurry has a concentration of from 18 wt% to 50 wt%;

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allowing the thus formed isobutylene rubber to exit the reactor while simultaneously allowing the feed-stream charging to continue.

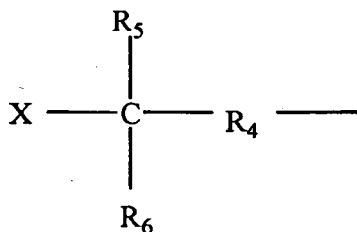
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58. The method of Claim 57, wherein the catalyst system is comprises a Lewis acid and an initiator in a polar diluent, the initiator having the formula:



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wherein X is a halogen; R_1 is selected from the group consisting of C_1 to C_8 alkyl, and C_2 to C_8 alkenyl; R_3 is selected from the group consisting of C_1 to C_8 alkyl, C_2 to C_8 alkenyl and phenylalkyl; and R_2 is selected from the group consisting of C_4 to C_{200} alkyl, C_2 to C_8 alkenyl, phenyl, phenylalkyl, alkylphenyl, C_3 to C_{10} cycloalkyl, and



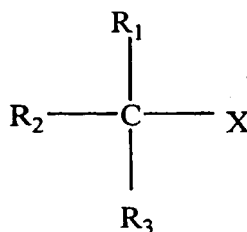
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wherein X is a halogen; R_5 is selected from the group consisting of C_1 to C_8 alkyl, and C_2 to C_8 alkenyl; R_6 is selected from the group consisting of C_1 to C_8 alkyl, C_2 to C_8 alkenyl and phenylalkyl; and R_4 is selected from the group consisting of phenylene, biphenyl, α,ω -diphenylalkane and --

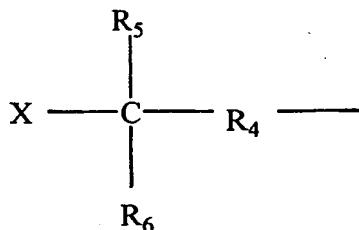
$(CH_2)_n$ -, wherein n is an integer from 1 to 10; and wherein R_1 , R_2 , and R_3 can also form adamantyl or bornyl ring systems, the X group being in a tertiary carbon position.

- 5 59. The method of Claim 58, wherein the slurry is present in the reactor in a range greater than or equal to 18 wt%.
60. The method of Claim 58, wherein the slurry is present in the reactor less than or equal to 50 wt%.
- 10 61. The method of Claim 58, wherein the polar diluent is selected from the group consisting of CH_3Cl , $EtCl_2$, CH_2Cl_2 , $CHCl_3$, CO_2 , CCl_4 and mixtures thereof.
- 15 62. The method of Claim 58, wherein the ratio of the Lewis acid to the initiator on a molar basis is from 1.1 to 2.0.
63. The method of Claim 58, wherein the ratio of the Lewis acid to the initiator on a molar basis is from 0.75 to 5.
- 20 64. The method of Claim 58, wherein the reaction generates heat conducted through the slurry, the slurry having a heat transfer coefficient.
- 25 65. The method of Claim 64, wherein the heat transfer coefficient of the slurry is from 200 to 500 Btu/hr·ft²·°F.
66. The method of Claim 64, wherein the heat transfer coefficient of the slurry is from 300 to 450 Btu/hr·ft²·°F.
- 30 67. The method of Claim 64, wherein the heat transfer coefficient of the slurry is from 375 to 450 Btu/hr·ft²·°F when the slurry concentration is from 25 to 30 wt%.

68. The method of Claim 64, wherein the heat transfer coefficient of the slurry is from 200 to 350 Btu/hr·ft²·°F when the slurry concentration is from 30 to 35 wt%.
69. A catalyst system comprising a Lewis acid and an initiator in a polar diluent, the initiator having the formula:

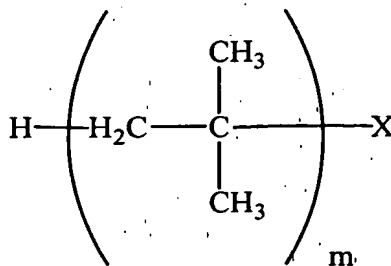


wherein X is a halogen; R₁ is selected from the group consisting of C₁ to C₈ alkyl, and C₂ to C₈ alkenyl; R₃ is selected from the group consisting of C₁ to C₈ alkyl, C₂ to C₈ alkenyl and phenylalkyl; and R₂ is selected from the group consisting of C₄ to C₂₀₀ alkyl, C₂ to C₈ alkenyl, phenyl, phenylalkyl, alkylphenyl, C₃ to C₁₀ cycloalkyl, and



wherein X is a halogen; R₅ is selected from the group consisting of C₁ to C₈ alkyl, and C₂ to C₈ alkenyl; R₆ is selected from the group consisting of C₁ to C₈ alkyl, C₂ to C₈ alkenyl and phenylalkyl; and R₄ is selected from the group consisting of phenylene, biphenyl, α,ω-diphenylalkane and --(CH₂)_n--, wherein n is an integer from 1 to 10; and wherein R₁, R₂, and R₃ can also form adamantyl or bornyl ring systems, the X group being in a tertiary carbon position.

70. The catalyst system of Claim 69, wherein the initiator is selected from the group having the formula:



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wherein X is a halogen and the value of m is from 1 to 60, and mixtures thereof.

71. The catalyst system of Claim 69, wherein the value of m is from 2 to 40.

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72. The catalyst system of Claim 69, wherein the initiator is selected from the group consisting of:

2-chloro-2-phenylpropane;

1,4-di(2-chloro-2-propyl)benzene;

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1,3,5-tri(2-chloro-2-propyl)benzene;

3-tert-isobutylene-1,5-di(2-chloro-2-propyl)benzene;

2-chloro-2,4,4-trimethylpentane;

2-bromo-2,4,4-trimethylpentane;

1-chloroadamantane;

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1-chlorobornane;

cumyl chloride;

2,6-dichloro-2,4,4,6-tetramethylheptane and mixtures thereof.

73. The catalyst system of Claim 69, wherein the polar diluent is selected from the group consisting of CH_3Cl , EtCl_2 , CH_2Cl_2 , CHCl_3 , CO_2 , CCl_4 and mixtures thereof.

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74. The catalyst system of Claim 69, wherein the polar diluent is CH_3Cl .
- 5 75. The catalyst system of Claim 69, wherein the ratio of the Lewis acid to the initiator on a molar basis in the diluent is from 1.1 to 2.
76. The catalyst system of Claim 69, wherein the ratio of the Lewis acid to the initiator on a molar basis in the diluent is from 0.75 to 5.
- 10 77. The catalyst system of Claim 69, wherein the Mn of the initiator is up to 2500.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/48194

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C08F 4/44, 4/52; C08F 110/10, 110/14

US CL : 502/152, 224, 227, 231; 526/90, 144, 206, 348.6, 348.7

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 502/152, 224, 227, 231; 526/90, 144, 206, 348.6, 348.7

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EAST

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,506,316 A (SHAFFER) 09 April 1996 (09.04.1996), col. 3, line 56 through col. 6, line 48.	1-20, 30-43, 45-50, 53-56, 69, 70, 72-77
X	US 6,074,978 A (SHAFFER) 13 June 2000 (13.06.2000), col. 2, line 14 through col. 5, line 17, col. 7-9.	1, 2, 8-10, 12-20, 40-43, 45-50, 54-56, 69, 70, 72-77

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search

25 March 2002 (25.03.2002)

Date of mailing of the international search report

18 APR 2002

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